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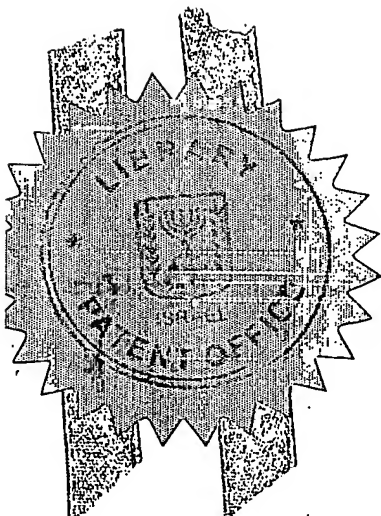
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ב ק ש ה ל פ ט נ ט  
Application for Patent

מספר: Number	152802
תאריך: Date	2-11-2002
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אני, (שם המבקש, מענו – ולגבי גוף מאוגד – מקום התאגדותו)  
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תהליך להמסת תחמוצת בריליום ממחצבים  
(בעברית)  
(Hebrew)

A METHOD FOR LEACHING BERYLLIUM OXIDE FROM ITS ORES  
(באנגלית)  
(English)

הממציאים: שמחה הראל, לב שפירא  
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A METHOD FOR LEACHING BERYLLIUM OXIDE FROM ITS ORES

תהליך להמסת תחמוצת בריליום ממחצבים

INVENTORS:

Simcha Harel

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## FIELD OF THE INVENTION

The present invention relates to a method for leaching beryllium oxide from its ores: beryl and/or bertrandite and /or phenakite.

## BACKGROUND OF THE INVENTION

Beryllium (Be) is one of the lightest of all metals and has one of the highest melting points of any light metal. Beryllium metal and its alloys are used principally in aerospace and defense applications because of its stiffness, light weight, and dimensional stability over a wide temperature range. This silver-colored, brittle metal is stiffer than 1010 steel, and is also highly conductive. Beryllium and its alloys are often the chosen materials for electronic equipment. Beryllium-copper alloys are used in a variety of applications because of their electrical and thermal conductivity, high strength and hardness, good corrosion and fatigue resistance, and nonmagnetic properties. Beryllium oxide is an excellent heat conductor, with high strength and hardness, and acts as an electrical insulator in some applications.

Today, beryllium is extracted from the minerals beryl, bertrandite and phenakite ores. Although solid beryllium poses no health hazard, inhaling beryllium particles or fumes can produce acute or chronic lung disease.

The domestic producer price for beryllium contained in beryllium-copper master alloy remained at \$160 per pound in 1998, since 1990. Prices for other forms of beryllium also have not changed in nearly a decade. Beryllium and beryllium alloys are very often the most expensive materials available for a given application.

The main ores, containing beryllium, are beryl and bertrandite. The composition of the Be-mineral, Beryl, is  $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ . Commercial Beryl contains about 12% BeO, which is close to the theoretical composition of beryl - 14%BeO. The composition of bertrandite is  $4\text{BeO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ , which according to the chemical composition contains 56%BeO. Commercial bertrandite contains about 0.6%BeO. While the beryl is almost a pure mineral, the commercial bertrandite contains 1.0-1.5% of the pure bertrandite, admixed with additional minerals such as aluminum and iron oxides, calcium and alkali oxides or silicates and quartz.

The metal beryllium and its compounds are very costly, due to several reasons:

The toxicity of beryllium: Chronic beryllium disease, or berylliosis, is an allergic reaction to beryllium which results in the lungs becoming inflamed and scarred, inhibiting oxygenation of the bloodstream. Symptoms include shortness of breath, dry cough, chest pain, fatigue, weight loss and loss of appetite.

The exposure for 8 hour work with beryllium should not exceed 2 micrograms of beryllium/m<sup>3</sup>. A brief exposure should not exceed 25 micrograms /m<sup>3</sup>. Tasting of solutions of beryllium compounds is not dangerous. Before atomic absorption was introduced in analytical chemistry, the solutions were tasted for sweetness. It is acknowledged in this respect that the term Beryllium is referred to in the German language as 'Glucinum'.

Production of Beryllium compounds from Beryl: The first step of the production of beryllium compounds from beryl, the beryllium oxide rich ore, is by melting the ore at 1,650°C.

The melted ore is quenched in water and once more heated to 900° to 950°C and cooled. After grinding to 200 mesh a slurry of the powder in concentrated sulfuric acid is heated to 250° to 300°C converting the beryllium and aluminum to soluble sulfates. The silica fraction remains in the dehydrated, water insoluble form. 90-95% of the beryl oxide content are dissolved.

There are other known complicated processes for the dissolution of beryllium oxide, such as alkali treatment, the fluoride and chloride processes, which are not simpler than the sulfuric acid process.

After the dissolution step of the beryllium oxide, many procedures are described in the literature for separating the beryllium sulfate from the other dissolved metal sulfates.

~~Further~~ details of the processes are described in Encyclopedia- Kirk- Othmer (Vol. 4, pages 126 to 138) and in Encyclopedia Ullmann, (Vol, 4a, pp. 15-26 ).

According to the present invention that will be described below, the beryllium oxide is leached from the ores in suspension by a selective reagent at a temperature of about 100°C. The expensive stage of melting the ore is not necessary. The leaching of

beryllium oxide from the raw materials is much cheaper than treatment by the other known processes.

#### Leaching of the beryllium oxide from bertrandite

As opposed to beryl, in the known commercial production process of the beryllium compounds from bertrandite, no melting step is necessary. According to the known process, sulfuric acid at boiling dissolves the beryllium, aluminum, iron, and other oxides of the ore. The solution is filtered to remove the insoluble silica from the solution. Many procedures for separation of the beryllium sulfate from the other sulfates are described in the literature. One of these is the use of liquid-liquid extraction of beryllium. Beryllium, aluminum and iron sulfate are extracted into the organic phase. By adding ammonium carbonate solution to the organic phase, beryllium hydroxide is precipitated. This is the Brush Wellmann process of beryllium compounds production from bertrandite. Though the process is quite complicated, the price of the beryllium compounds is high enough to compensate for the expensive production process.

#### SUMMARY OF THE INVENTION

It is thus the scope of the present invention to present a useful method for obtaining soluble beryllium compounds from ores containing beryllium. Said ores are preferably selected from beryl, bertrandite, or phenakite or other beryllium containing ores. The hereto-defined method is essentially characterized by a mixing step, wherein a suspension of said ores is effectively mixed with fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ). It is especially in the scope of the present invention, wherein said mixing step comprises of leaching the suspension of beryllium ores by fluosilicic acid for 2 to 6 hours at about  $100^\circ\text{C}$  so that 80% to 100% of the beryllium is dissolved. Consequently, beryllium fluoride and other soluble fluorides may thus be produced. In addition, the method may comprise of a step of filtering the obtained leached solutions from the insoluble materials. Similarly, the method may also comprise the step of obtaining pure amorphous silica from a vapor phase, wherein fluosilicic acid is recovered and reused.

It is also in the scope of the present invention, wherein the fluosilicic acid is at least partially reused and/or recycled. Thus, according to one preferred embodiment of the present invention, said method may comprise the following steps: (a) mixing a suspension of said ores with fluosilicic acid so that 80% to 100% of the beryllium oxide is dissolved to beryllium fluosilicate; (b) heating the solution obtained in the previous step, to obtain soluble beryllium fluoride, and partly soluble aluminum and ferric fluorides; (c) filtering the said heated solution from the insoluble residue, comprising quartz and insoluble metal fluorides; and (d) evaporating the silicon tetra fluoride obtained in step (b) to yield amorphous silica and fluosilicic acid to be reused in the mixing step (a).

#### BRIEF DESCRIPTION OF THE INVENTION

In order to understand the invention and to see how it may be carried out in practice, a preferred embodiment will now be described, by way of non-limiting example only, with reference to the accompanying drawing, in which Figure 1 schematically presents a block diagram of the proposed process.

#### DETAILED DESCRIPTION OF THE INVENTION

It is the primary goal of the present invention to present a novel and useful method for leaching beryllium oxide from its ores. Thus, according to the present invention, fluosilicic acid also denoted in the present invention in the chemical term  $\text{H}_2\text{SiF}_6$ , dissolves beryllium oxide from the suspension of the ore (beryl, bertrandite, phenakite or any other beryllium containing ores) at a temperature close to  $100^\circ\text{C}$ . In the known process for the production of beryllium compounds from beryl (as described above) the thermal treatment is very expensive, while the leaching of the beryllium oxide from the ore by fluosilicic acid at a temperature near  $100^\circ\text{C}$  is much cheaper. This is the first advantage of the proposed process.

In other known processes, excess of concentrated sulfuric acid is used which must be later neutralized in the process. The leaching of the beryllium oxides from the ores proceeds according to the proposed process, at a temperature near  $100^\circ\text{C}$  while the leaching by sulfuric acid occurs at  $250^\circ\text{C}$ . This is the second advantage of the proposed process.

The third advantage of the use of fluosilicic acid according to the proposed process is, that instead of using sulfuric acid and neutralizing it later in the process, the use of fluosilicic acid enables the by- production of pure amorphous silica and the recovery of the fluosilicic acid. By heating fluosilicic acid, (in absence of silica) hydrofluoric acid and silicon tetrafluoride evaporate and by cooling the vapors, fluosilicic acid is restored. In presence of silica, only the more volatile silicon tetra fluoride evaporates, the hydrofluoric acid remains in the solution and dissolves the silica, whereby fluosilicic acid is produced. The vapors of silicon tetrafluoride and water , produce by cooling, amorphous silica and fluosilicic acid.

There are two kinds of silica in the ores: Quartz, and amorphous silica. The quartz is insoluble in the fluosilicic acid.

The amorphous silica is soluble and dissolved in the fluosilicic acid. The addition of sulfuric acid to the fluosilicic acid enhances the dissolution of beryllium.

After filtration of the solution, any process known from the literature can be used for the production of various beryllium compounds from it. Aluminum oxide, iron oxide and other metal oxides also dissolve in the fluosilicic acid, produce fluosilicates of these metals, and by heating, their fluorides are obtained. Some of these fluorides are partly insoluble such as  $\text{AlF}_3$ ,  $3\text{H}_2\text{O}$ ,  $\text{FeF}_3$  and  $\text{NaF}$ .

Other fluorides such as  $\text{CaF}_2$ ,  $\text{MgF}_2$ , and silica in the form of quartz are insoluble.

When the ores contain sodium and potassium, they will be in the beryllium fluoride solution, from which the beryllium hydroxide is precipitated by alkali .

No work was carried out so far, on how to proceed with the separation of beryllium from the solution. The main goal of the claimed process is to obtain the simple dissolution of the beryllium oxide from its ores. Any process known from literature for the production of a beryllium compound from its solutions suits for this purpose.



## THE THEORETICAL EXPLANATION OF THE INVENTION

Three patent applications appeared lately,

1. Isr. 140,646 – The production of aluminum salts from clay
2. Isr. 144,038 – The production of aluminum fluoride from clay and coal ash.
3. Isr. 148, 376 – Production of pure amorphous silica from silica containing ores.

According to the first and second processes, fluosilicic acid dissolves aluminum oxide selectively from ores such as clay at a temperature of  $60^{\circ}$ - $70^{\circ}$ C. A solution of aluminum fluosilicate is obtained, from which aluminum sulfate is obtained by the reaction with sulfuric acid, and aluminum fluoride is obtained by heating the solution of aluminum fluosilicate.

According to the third process, pure amorphous silica is produced from any raw material containing silica in the amorphous form or as silicate (not quartz) by heating with fluosilicic acid at a temperature close to  $100^{\circ}$ C.

In this invention, it is claimed that the fluosilicic acid dissolves beryllium oxide, as the examples further describe. Practically, no dissolution of beryllium oxide was achieved, at  $60$ - $70^{\circ}$ C. By raising the temperature to  $100^{\circ}$ C the beryllium oxide dissolved. Both steps of leaching aluminum oxide by fluosilicic acid at  $70^{\circ}$ C, and production of pure silica at  $100^{\circ}$ C, happen simultaneously at  $100^{\circ}$ C with the beryllium ores.

The theoretical quantity of fluosilicic acid needed to dissolve the beryllium oxide from the ores, must be calculated from the cations of the ore as well as from its silica content (amorphous silica - not quartz).

Practically, a larger excess of fluosilicic acid must be used to achieve the dissolution of the beryllium oxide. However, in addition to the production of amorphous pure silica, the excess fluosilicic acid is recovered.

By boiling the fluosilicic acid, silicon tetra fluoride and hydrofluoric acid are evaporated. When the silica is present in the suspension, either amorphous or as

silicate, the hydrofluoric acid dissolves the silicon dioxide. By cooling the vapors, amorphous silica is produced and the fluosilicic acid is regenerated.

## EXAMPLES

As stated above, in order to understand the invention and to see how it may be carried out in practice, a plurality of preferred embodiments will now be described, by way of non-limiting examples only. Those embodiments clearly show that practically 100% of the beryllium oxide from bertrandite is dissolved by the described process. Similarly, up to 80% of the beryllium oxide was leached from beryl.

## EXPERIMENT 1

Bertrandite of the following composition was used: 0.63%BeO, 11.89% Al<sub>2</sub>O<sub>3</sub>, 3.69%CaO, 1.48%Fe<sub>2</sub>O<sub>3</sub>, 3.97%K<sub>2</sub>O, 1.79%MgO, 2.89%Na<sub>2</sub>O, 66.44%SiO<sub>2</sub>, 2.16%F

25g of the above sample of bertrandite were suspended in 185 g of 24.5% fluosilicic acid, the suspension stirred and heated for 2 hours at 98°C, then the suspension was cooled, filtered and washed. The volume of the filtrate and the washing was 330 ml. The solution was analyzed for beryllium and 468mg BeO per liter was found. The weight of the wet residue was 33.86g, and after drying 18.93g.

The residue consists of quartz , insoluble fluorides as calcium and magnesium fluoride, and some partly insoluble fluorides , as aluminum and ferric fluorides.

25g of bertrandite of 0. 63 % BeO:	→	25 x 0.63x10	= 157.5 mg BeO
mg BeO found in Exp.1	→	468 x 0.330	= 154.4 mg BeO
% of BeO dissolved : 154.4 x 100 / 157.7 = 98.1%			

The aim of the experiments was not the production of a pure beryllium compound. This can be obtained by use of any procedure from the literature or by a procedure to be specifically worked out for this solution.

## EXPERIMENT 2

25g of bertrandite were suspended in 184g of fluosilicic acid (24.5% H<sub>2</sub>SiF<sub>6</sub>). The suspension was stirred and heated for 1 hour at 70°C , cooled, filtered and washed. The volume of the filtrate and the washing was 386 ml.

The weight of the residue after drying was 18.6g. The solution contained 369mg BeO per liter.

Mg BeO found :  $38.6 \times 0.369 = 142\text{mg BeO}$ .

% BeO dissolved :  $142 \times 100/157.5 = 90.3\%$

### EXPERIMENT 3

15g of bertrandite were suspended in 109g of fluosilicic acid (24.5%  $\text{H}_2\text{SiF}_6$ ). The suspension was stirred and heated for 0.5 hour at  $72^\circ\text{C}$ . After cooling filtering and washing, 254ml of solution was obtained. The solution contained 330.6ml BeO per liter.

BeO found :  $330.6 \times 0.254 = 84.0\text{mg}$ .

BeO in sample :  $15 \times 0.63 \times 10 = 94.5\text{mg}$

%BeO dissolved :  $84.0 \times 100/94.5 = 88.9\%$

### EXPERIMENT 4

Beryl of the following composition was used: 12.18% BeO, 0.03% CaO, 0.86%  $\text{Fe}_2\text{O}_3$ , 0.73%  $\text{Na}_2\text{O}$ , %F-n.r., 17.44%  $\text{Al}_2\text{O}_3$ , 0.02% CdO, 0.22% CoO, 0.12% MgO, 1.63%  $\text{P}_2\text{O}_5$ , 0.39% PbO, 64.45%  $\text{SiO}_2$ , 0.03%  $\text{TiO}_2$ , 0.42%  $\text{Cr}_2\text{O}_3$ , 0.00% CuO, 2.98%  $\text{In}_2\text{O}_3$ , 0.17% MoO, 0.07% NiO, 0.03%  $\text{V}_2\text{O}_5$ , 0.15%  $\text{Y}_2\text{O}_5$ , 0.01% ZnO, 0.00% ZrO.

15 g of the sample were suspended in 185 g of fluosilicic acid (24.5%  $\text{H}_2\text{SiF}_6$ ), the suspension stirred and heated to  $60^\circ\text{C}$  for 2 hours, and the insoluble residue was filtered off. The filtrate was analyzed for beryllium. 34 mg BeO dissolved from the total 1.815 g BeO in the sample, this being 1.87% of the total.

Remark: The low temperature of  $60^\circ\text{C}$  used in the experiment, is the temperature at which aluminum oxide content of clay dissolves. The result showed clearly, that at this temperature beryllium oxide from beryl is hardly dissolved.

### EXPERIMENT 5

The exp. 4 was repeated at  $94^\circ\text{C}$ : 15 g of the beryl containing 1.815 g BeO was used. 0.398g of beryllium oxide dissolved within two hours. 21.9% of the beryllium oxide dissolved. The insoluble residue was 9.89g

#### EXPERIMENT 6

As in Exp.5, but 463g of fluosilicic acid was used. The duration of the experiment was 4 hours. The temperature was 102°C.

40.7% of the beryllium oxide dissolved. The insoluble residue: 8.40g

#### EXPERIMENT 7

As in Exp.6, but 488g of fluosilicic acid and 50 g of sulfuric acid were used, time of reaction 5 hours, the temperature kept at 107°C. 61.8% of the beryllium oxide dissolved. The insoluble residue : 8.76g

#### EXPERIMENT 8

As in Exp.7, but 594 g of fluosilicic acid was used, no sulfuric acid added, duration of the reaction 5 hours at 103°C.

Though no sulfuric acid was used 56.7% dissolution of the beryllium oxide was achieved. The insoluble residue: 7.32g

#### EXPERIMENT 9

As in Exp.8, using 15 g of finely ground beryl; and 724 g of fluosilicic acid (24.5%  $\text{H}_2\text{SiF}_6$ ) was used, duration of the heating 6 hours at 103°C. The suspension was filtered.

The weight of the filtrate and washing was 228 g, containing 6.055 g BeO / liter solution. The weight of the dried residue was 7.32 g.

The insoluble residue: 8.06g

Beryllium oxide dissolved:  $6.055 \times 0.228 = 1.38\text{g}$ .

% BeO dissolved =  $1.38 \times 100 / 1.815 = 76.1\%$

Adding time of dissolution enhances the dissolution of the beryllium oxide. Adding sulfuric acid yields better dissolution of the beryllium oxide.

## CLAIMS

1. A method for obtaining soluble beryllium compounds from ores comprising beryllium; characterized by mixing a suspension of said ores with fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ).
2. The method according to claim 1, wherein said mixing step comprises of leaching the suspension of beryllium ores by fluosilicic acid for 0.5 to 6 hours at  $60^\circ\text{C}$ – $120^\circ\text{C}$  so that 80% to 100% of the beryllium is dissolved.
3. The method according to claim 1, comprising a step of filtering the obtained leached solutions from the insoluble materials.
4. The method according to claim 3, comprising the step of obtaining pure amorphous silica from the vapor phase, wherein fluosilicic acid is recovered and reused.
5. The method according to claim 2, wherein the solution contains beryllium fluoride and other soluble fluorides as obtained by the leaching process.
6. The method according to claim 1, wherein the fluosilicic acid is at least partially reused and/or recycled.
7. The method according to claim 6 adapted to mixing the ores containing beryllium with recycled fluosilicic acid comprising;
  - i. mixing a suspension of said ores with fluosilicic acid so that 80% to 100% of the beryllium oxide is dissolved to beryllium fluosilicate.
  - ii. heating the solution obtained in the previous step, to obtain soluble beryllium fluoride, and partly soluble aluminum and ferric fluorides;
  - iii. filtering the said heated solution from the insoluble residue, comprising quartz and insoluble metal fluorides.
  - iv. evaporating the obtained silicon tetra fluoride to yield amorphous silica and fluosilicic acid to be reused in the mixing step. .
8. The method according to claim 1, wherein the suspension of the ores is mixed with a predetermined mixture of fluosilicic acid and sulfuric acid.
9. The method according to claim 1, wherein the ores are selected from beryl, bertrandite, or phenakite.

*Signature*

FIGURE 1

